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Acid Deposition
Processes of Lake Acidification

National Research Council, Washington, DC

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March 5, 1984

Panel on Processes of Lake Acidification
Environmental Studies Board
Commission on Physical Sciences, Mathematics, and Resources
National Research Council

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PANEL ON PROCESSES OF LAKE ACIDIFICATION

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*Because of illness, the chairman was unable to participate in the early part of the discussion. With the concurrence of the chairman, James Galloway served as acting chairman.
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PREFACE

The Panel on Processes of Lake Acidification was formed under the auspices of the Environmental Studies Board of the National Research Council (NRC) at the request of the Environmental Protection Agency (EPA). The panel was convened to discuss a series of questions posed by EPA about lake acidification processes. The panel met on March 5, 1984.

This report is a summary of that discussion. The report includes a brief overview of current understanding of the processes of lake acidification, a discussion of the questions, and conclusions, where they could be reached, on aspects of lake acidification. This report is then more like the proceedings of a symposium rather than the more typical NRC report, which normally reflects the deliberations and scientific consensus of a committee over a period of time.

The summary was prepared by the panel shortly after the meeting. I want especially to acknowledge the contributions of James Galloway and Richard Wright in this regard. They shouldered the major burden of preparing the final version accommodating revisions suggested by the other panel members.

Finally, I wish to thank the members of the panel for their cooperation in responding on very short notice to EPA's request and for their dedication to the project. William Stigliani and Joyce Fowler, of the Environmental Studies Board staff, also earned the appreciation of the panel and the board for their efforts in organizing the panel and supporting its deliberations.

Stanley I. Auerbach, Chairman
Environmental Studies Board

INTRODUCTION

The Panel on Processes of Lake Acidification was assembled by the National Research Council at the request of the Environmental Protection Agency (EPA). The panel was charged with discussing the processes that control the rate of acidification of streams and lakes and to suggest how EPA's research program might approach addressing current deficiencies in knowledge.

The panel defined the acidification of lakes and streams as a decrease in alkalinity over time. Soil acidification is the decrease in the percent base saturation (%BS) over time. The panel concurred that in forested watersheds that are underlain by granitic or other highly siliceous bedrock with acidic forest soils not receiving appreciable acid deposition, most lakes and streams have bicarbonate as the dominant anion and pH levels above 5.5. Generally, lakes and streams in similar habitats but in areas receiving appreciable acid deposition have sulfate as the dominant anion.

ACIDIFICATION HYPOTHESIS

James N. Galloway was asked to present his views on a general acidification hypothesis. This section summarizes his presentation, which was given at the beginning of the discussion.

Acidification of surface waters by acid deposition is a sequential process in three steps:

1. Sulfur deposition increases.
2. Sulfate concentrations in streams and lakes increase.

3. Concentrations of protolytic (H^+, Al^{n+}) and nonprotolytic (e.g., Ca^{2+}, Mg^{2+}) cations increase. The increases in protolytic cations cause decreases in stream and lake alkalinity.

The three steps are generally sequential, but in some cases steps 2 and 3 are simultaneous (i.e., in extremely acid soils). Each step has its own rate, which influences the succeeding step, as the following discussion shows.

Step 1: Increases in emissions of SO_2 cause increases in sulfur deposition.

Step 2: The sulfate concentrations in the streams and lakes begin to increase. The rate of the increase in sulfate depends primarily on the sulfur deposition rate and the sulfate adsorption capacity of the watershed. Sulfate concentrations in the streams and lakes will continue to increase until the watershed is in equilibrium with the higher sulfur deposition rate. In soils with a low sulfate adsorption capacity (such as is found in areas of the northeastern United States), streams and lakes will reach new equilibrium concentrations of sulfate in 1 to 10 years. In soils with moderate to high sulfate adsorption capacity (such as those found in areas of the southeastern United States), the sulfate concentrations of streams and lakes will continue to increase for periods of the order of decades to centuries. In addition to sulfate adsorption in soils, there are other sulfur sinks in soil (e.g., living biomass) that can cause additional delays in the response of a stream or lake to increases in sulfur deposition. For purposes of this discussion, however, only sulfate adsorption is considered.*

Step 3: As the sulfate levels in the streams and lakes increase, the concentrations of all cations (H^+, Al^{n+}, Ca^{2+}, Mg^{2+}) must also increase to varying degrees. If the concentrations of H^+ and Al^{n+} increase, then the stream or lake loses alkalinity and by definition becomes acidified. In general, lakes and streams associated with

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*In the discussion following Dr. Galloway's opening remarks, the panel identified biological transformations as a fourth process that may control acidification of lakes and streams. Dr. Galloway did not focus his discussion on biological transformations, but acknowledges their importance as a major process.

watersheds having hydrologic flow paths through acid soils will have the increase in sulfate predominately matched by an increase in H^+ and Al^{n+}.

The rate of acidification depends on the rate of change in sulfate concentrations in the water bodies and the soil characteristics of the watershed surrounding the streams or lakes. The important soil characteristics are controlled by the size of the cation exchange pool, the percent base saturation (%BS) of the cation exchange pool, and the rate of base cation supply to the cation exchange pool from other cation reservoirs (primary and secondary minerals).

Streams and lakes associated with soils with a low %BS and a moderate base cation supply rate will lose alkalinity as aqueous sulfate ($SO_4^=$) concentrations increase, but as $SO_4^=$ concentrations stabilize, alkalinity also stabilizes. Streams and lakes associated with soils with low %BS and a low base cation supply rate will not only lose alkalinity as sulfate concentrations increase but could also continue to lose alkalinity after the sulfate concentrations have stabilized due to decreases in the %BS of the soil.

Dr. Galloway concluded his summary of the lake acidification hyposthesis with the caution that questions still remain about the rates at which the processes affect lake acidification, in particular the base cation supply to the cation exchange pool. This ignorance limits our ability to predict how much and how fast streams and lakes will respond to changes in sulfur deposition.

DISCUSSION OF SPECIFIC QUESTIONS

Following Dr. Galloway's opening remarks, the panel discussed the questions posed by EPA. This section is a summary of that discussion.

1.a. Have lakes and streams become more acidic over the last 15 years? Different lakes and streams respond differently to a given loading of acid deposition. Fifteen years is too short a period over which to evaluate trends in the acidity of surface waters. The processes dominating surface water acidification have response times of years to decades. Given the natural year-to-year variability due to such factors as precipita-

tion amount, the changes due to acid deposition may be obscured.

However, it was generally agreed that from preindustrial times to the present in areas with sufficiently acid, shallow soils (i.e., soils whose hydrologic residence times are limited) increases in sulfur deposition have led to the acidification of surface waters. Many areas may be affected only slightly or not at all, however, because their soils are not sufficiently acid or there is adequate retention of solution with the mineral soil to accomplish neutralization. The magnitude of the response depends on a number of characteristics of the watershed and its soil as well as the magnitude of change in acid deposition.

1.b. Have the biota of lakes and streams changed over the last 15 years? The biological data from which changes due to acid deposition can be projected are of three types:

- toxicity experiments in the laboratory,
- experimental manipulations of water composition in the field, and
- survey data in which the biota in acidified clearwater lakes and streams are compared with the biota of nonacidified lakes and streams.

Information collected from these types of studies indicates that if lakes and streams have been acidified by acid deposition then biological effects will follow. Because the chemical changes are for the most part gradual and variable, 15 years is too short a period over which to evaluate biological trends. However, streams and lakes acidified by acid deposition have a different biotic structure than nonacidified streams and lakes.

Various organisms and groups of organisms present in lakes and streams can respond differently over time to changes in water chemistry. Thus the biota may still be responding to past changes in water chemistry.

2. To what extent have lakes and streams been acidified by acid deposition as opposed to other factors? Acidification of clear lakes and streams is caused by the atmospheric deposition of strong acid anions (sulfate and nitrate) on sufficiently acid, shallow soils.

Soil acidity is assumed to be the result of the cumulative effects of natural processes acting over many centuries. The extent to which acid deposition has contributed to soil acidity is quantitatively unknown. However, an acid soil itself does not necessarily produce acid streams or lakes. To produce streams and lakes that are acidified by acid deposition, both acid soils and acid deposition are required. The extent to which surface waters have been acidified by atmospheric deposition remains a topic for research.

3.a. What processes control surface water acidification? There was general agreement among the panel members that four major processes control acidification of lakes and streams:

- Acidity and amount of deposition.
- The release of base cations to the water flowing through the soil.
- Retention of sulfate by the watershed.
- Biological transformations within the terrestrial and aquatic systems.

In general, there are two pools of base cations in soils. The base cations on the cation exchange complex react very rapidly with soil solution. The release of base cations from primary and secondary minerals and biomass proceeds much more slowly. A major question is how rates of release from the slow pool are affected by changes in acid deposition.

The retention of sulfate in ecosystems occurs by sorption and biological processes. The extent of sulfate retention depends on factors such as the chemical composition of the soil, temperature, vegetation type and growth, and soil depth. Acidification of lakes and streams depends on the amount of sulfate or other strong acid anions such as nitrate leaving the soil and entering stream and lake water. In watersheds with a high sulfate retention capacity, as acid deposition continues, the ability of the watershed to retain additional inputs of sulfate diminishes, and stream and lake water concentrations of sulfate increase. Alkalinity will decrease if increases in sulfate are not matched by an equivalent increase in base cations.

Biological processes within watersheds cycle base cations and strong anions such as sulfate and nitrate. The biological processes, and particularly the

disturbance of them, can therefore influence the supply of base cations and the amount of sulfate and nitrate leaving the soil.

In addition to the four major processes, a myriad of other processes may have an influence on the chemistry of individual lakes or streams.

The relative importance of the last three processes given above depends in part on hydrologic pathways. Watersheds with deep seepage typically produce more alkaline waters.

3.b. Is the acidity of lakes and streams limited by the rate of acid deposition (rate limited) or by the capacity of the watershed to neutralize or retain acid deposition on a sustained basis (capacity limited)?* Does the watershed deteriorate in its capacity to absorb acid inputs? The panel determined that watersheds can be grouped according to their characteristics with respect to two processes--the ability to retain sulfate and the ability to supply base cations. The lakes and streams whose watersheds have both a low ability to retain sulfate inputs and a low ability to release base cations fall in the lower right-hand corner of Figure 1. These lakes and streams respond rapidly to changes in acid deposition. Lakes and streams associated with watersheds having a high ability to retain sulfate but low ability to supply base cations will acidify at slower rates. Lakes and streams associated with watersheds having a high ability to supply base cations are capacity "protected" from acid deposition.

Watersheds with low base cation release rates and high sulfate retention capacity theoretically can deteriorate in their ability to adsorb acid inputs. As acid inputs

*Most panel members said the terms "rate limited" and "capacity limited" lacked clarity. They suggested that better descriptive terms for rates of lake and stream acidification are quick response (on the order of a few years to 20 years based on a few mean residence times of water in the most sensitive lakes and streams); delayed response (on the order of decades or longer based on the sulfate sorption capacity of the watershed); and no response (on the order of centuries or millennia). The original terms are preserved in the questions because they are the language used in the questions posed to the panel.

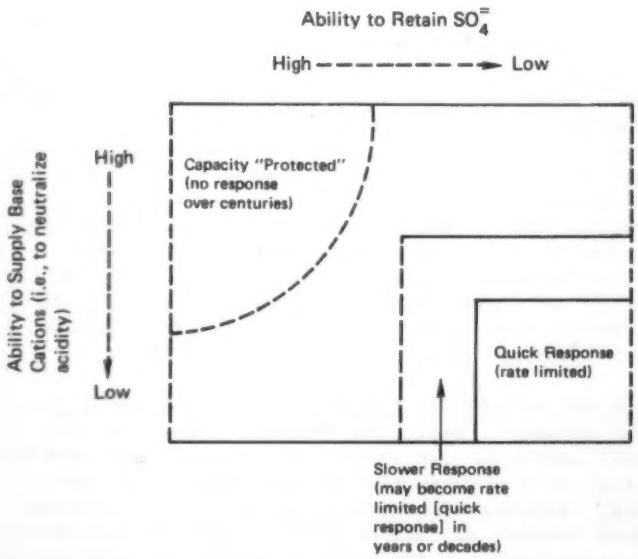
Ability to Retain $SO_4^=$
High
Low
Ability to Supply Base Cations (i.e., to neutralize acidity)
High
Low
Capacity "Protected" (no response over centuries)
Quick Response (rate limited)
Slower Response (may become rate limited [quick response] in years or decades)

FIGURE 1 A qualitative presentation of the effect of two major soil properties--the ability to retain sulfate and the ability to supply base cations--on the rate at which streams and lakes respond to changes in acid deposition.

continue, less and less of the deposited sulfate would be retained, and the stream and lake water would become increasingly acidified. Schematically, the size of the box labeled "Slower Response" in the lower right-hand corner of the figure becomes wider with time. The rate at which that box becomes larger depends on the sulfate retention capacity, the sulfate deposition rate, and the ability of the watershed to release base cations.

4. How do the rate-controlling processes or capacity-controlling processes for surface water acidification differ between regions? In areas of the northeastern United States (or in any area with watersheds having low ability to retain sulfate) that have sufficiently acid, shallow soils, lakes and streams can be expected to respond quickly to changes in acid deposition. Here rate-controlling processes dominate. In the Southeast (or any area with soils having high ability to retain

sulfate), on the other hand, the response is generally slower because of the typically high sulfate retention ability of the soils. Here capacity-controlling processes dominate. Generally, low-alkalinity lakes and streams in the mountainous West and upper Midwest are similar to lakes and streams in the Northeast in that they also are dominated by rate-controlling processes. Exceptions can be found in all regions.

Generally, any stream or lake with a small watershed to lake area ratio will be expected to respond more quickly to changes in acid deposition because of the predominance of direct inputs from acid deposition onto the surface of the lake as opposed to indirect inputs from water passing through the surrounding soil.

5. Is the concept of target loading applicable to lakes and streams? Yes. The "target" should be the biological health of the lakes and streams. The chemical composition of the lakes and streams determines the biological response with respect to changes in acidity. The target loading is thus defined as the maximum amount of acid deposition a given lake or stream can receive and still maintain a chemical composition at all times such that the biological health is unimpaired. Target loadings can be estimated for individual lakes and streams and groups of similar lakes and streams. The delay in the response will vary, as the panel has addressed in questions 1 through 4.

6.a. How would currently acidified lakes in the eastern United States respond to substantially lower levels of acid deposition? The panel agreed that, in general, the now-acid clearwater lakes and streams are those whose acidity is limited by the rate of acid deposition. These systems have responded to increases in acid deposition in the past and will respond to future changes in acid deposition. In watersheds that retain significant quantities of sulfate, lakes and streams that have responded more slowly to acid deposition will continue to respond to past levels of acid deposition and will exhibit slow response to any future increases or decreases in acid deposition.

6.b. How would low-alkalinity lakes in the upper Midwest and western United States respond to higher levels of acid deposition? In general, low-alkalinity lakes and streams in the upper Midwest and mountainous

West would be expected to respond rapidly to increases in acid deposition. If the soils are sufficiently acid and shallow, acidification of lakes and streams will result. The magnitude of response of lakes and streams will depend on the the flow path of water, the ability of their watersheds to retain acid anions, and the ability of the soils to supply base cations.

6.c. How would currently acidified lakes and streams in the eastern United States respond to unchanged levels of acid deposition? There was a lack of consensus from the panel on the rate of change in alkalinity in lakes and streams with continued constant sulfur deposition in the Northeast or for any other area with watersheds having a low ability to retain sulfate.

The two positions were as follows:

- Once watersheds are saturated with respect to sulfur, further decreases of alkalinity will be zero or gradual over periods of centuries, or
- Once watersheds are saturated with respect to sulfur, further decreases of alkalinity will still be noticeable owing to the continued net loss of base cations from ion exchange sites.

Note that the members of the panel agree on the processes. The disagreement is on the rate of the processes. To resolve this issue, both field and laboratory studies on the rate of supply of base cations to the ion exchange pool are required.

In the southeastern United States the sulfate concentrations in lakes and streams are thought generally to be increasing; in those areas with sufficiently acid, shallow soils these increases are ultimately accompanied by decreases in alkalinity. However, in areas where soils are not sufficiently acid, the increases in sulfate will result in increases in base cations.

7. What research is necessary to better answer questions 2 through 6? More information is needed on the rates at which the four major processes control lake and stream acidity. In particular, information on how the ability of natural systems to supply base cations and remove strong acid anions changes with time is critical to predict the effects of changes in the acidity of atmospheric deposition. Current research conducted by

the EPA and other organizations may already be addressing these questions.

Knowledge of the rate at which the replenishment of base cations to soil exchange sites proceeds is of critical importance. Research might include laboratory experiments with soil columns, intensive studies at gauged watersheds, and analysis of long-term trends in existing data.

We also need additional information on sulfate retention. For example, is sulfate retained in the watershed by reduction, vegetation uptake, adsorption, or chemical precipitation?

A small number of gauged watersheds and lakes should be carefully chosen and dedicated to the intensive study of atmospheric inputs, soil and vegetation processes, and runoff outputs. A long-term commitment is necessary. The Hubbard Brook Ecosystem Study (which has been supported by the U.S. Department of Agriculture Forest Service and the National Science Foundation since 1963) is an excellent example.

8. Are monitoring programs appropriate and warranted for detecting changes that might take place? What are the essential elements of such programs if they are desirable? Is an early warning monitoring system practical? Yes, monitoring programs and an early warning monitoring system are vital. Again, a series of carefully selected watersheds and lakes should be monitored intensively with the goal of registering both short- and long-term changes in deposition, soils, terrestrial vegetation, aquatic chemistry, and aquatic biota. Such monitoring might also include other pollutants deposited from the atmosphere, such as trace metals and organic compounds.

CONCLUSIONS

1. There is empirical and theoretical evidence for lake and stream acidification.
2. In the United States, there are rate-limited and capacity-limited lakes and streams. It should be noted, however, that a continuum between both types of systems is found in all regions of the United States.
3. The major processes that control the rate of acidification of lakes and streams are (a) the quality

and quantity of acid deposition, (b) base cation supply rate to the ion exchange pool, (c) sulfate retention in watersheds, and (d) biological transformations. Our lack of knowledge of (c), (d), and especially (b) is currently limiting our ability to predict acidification rates in individual lakes and streams.

4. Theoretically, in lakes and streams impacted by acid deposition, where sulfate concentrations are still increasing, the alkalinity will continue to decrease.

5. With respect to lakes and streams affected by acid deposition, where sulfate concentrations are stable, there is disagreement in the panel as to whether future alkalinity decreases will be gradual over the period of centuries or perceptible over years to decades. The disagreement stems from a lack of data.

6. For areas where adequate data on lake and stream composition and pertinent soil characteristics exist, we can <u>estimate</u> how the lakes and streams will change with time and with changes in the acidity of deposition.

7. Once we improve our understanding of the factors that control base cation supply rate, we will be able to <u>predict</u> with greater certainty how streams and lakes will change with time.